Review

Sources, Indicators, and Assessment of Soil Contamination by Potentially Toxic Metals

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Abstract: Soil pollution caused by potentially toxic metals has become a worldwide environmental issue. Geogenic processes and anthropogenic activities are two important sources of soil pollution. Soils may inherit toxic metals from parent materials; however, soil pollution mostly results from industrial and agricultural activities. Contamination by metals can be indicated by the changes in chemical, biochemical, and microbial properties of soils and plant responses. The total concentration of toxic metals in soil is still the most widely used indicator for risk assessment although extractable amounts have been reported to be more closely related to plant uptake. Several models have been proposed for assessing soil contamination by toxic metals, but none of them are commonly accepted for application to a wide range of soils. This review paper highlights how toxic metal contamination negatively affects soil and environmental quality, impacts food quality and security, and poses a threat to human health. Further research is needed to not only improve soil contamination diagnosis, modeling, and regulatory standards but also for remediation efficiency.

Keywords: assessment models; pollution sources; regulatory standards; soil contamination indicators; toxic metals

1. Introduction

It is estimated that 9 million people die annually from the toxic pollutants in air, water, and soil, which represents 16% of all deaths worldwide [1]. In all the environmental components, soil, as the largest natural filter for both inorganic and organic contaminants, plays a pivotal role in mitigating environmental pollution such as water and air pollution; however, soil could also become a source of pollution after it is saturated with contaminants [2–4]. Toxic metals are elements that are undegradable and consequently persistent in the environment and have the characteristics of ductility, conductivity, and ligand specificity with an atomic number >20 [5]. The most common contaminants of toxic metals are cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), arsenic (As), zinc (Zn), nickel (Ni), and lead (Pb) [6]. The presence of these contaminants in the soil can result in their transfer (and toxicity) to plants, animals, and humans. Soil pollution can be invisible, it affects humans slowly over a long period of time, and it becomes toxic to organisms within a short period under certain circumstances [2].

Soil heavy metal pollution has become a worldwide environmental issue that has posed a threat to human health. Among them, Cd is the most common pollutant, accounting for 7% of the total contaminated soils, followed by Ni, As, Cu, Hg, and Pb according to Chinese standards of soil contamination [7]. In China, it has been estimated

that approximately 150 thousand tons of farm products, including 50 thousand tons of rice (representing 0.025% of the global rice production), have been polluted by Cd each year [8]. It is important to mention that Cd-contaminated rice is a worldwide issue, not just in China. In Bangladesh, the populations with high rice consumption have an elevated intake of Cd as a result of the irrigation of rice paddies with Cd-contaminated groundwater [9]. In South America, cocoa exports have played an important role in the economy of countries such as Ecuador since it is an important ingredient of chocolate [10]. However, studies indicated that soil contamination has resulted in significant Cd accumulation in cocoa beans with twelve out of fifteen field sites having Cd concentration in cocoa beans exceeding the critical value (0.6 mg kg^{-1}) established by the European Union [10]. In addition, the Cd baseline levels for soil differed between countries [11]; for instance, it is 1 mg kg^{-1} in UK at pH 6 but is 20 mg kg^{-1} in Australia for residential areas. Efforts need to be made to develop international standards for soil pollution with potentially toxic metals.

The extent of soil contamination is also somewhat differing around the world. In China, 26 million ha of arable land were polluted by toxic metals including Cd, Pb, Hg, and As, and approximately 12 million metric tons of grains are being contaminated every year due to soil pollution, resulting in economic losses exceeding USD 3.2 billion [4,12,13]. In 2014, the Ministry of Environmental Protection of China released a soil survey report, showing that 16% of the agricultural soils were contaminated, with 82.8% being polluted by inorganic contaminants [7]. In the European Union, it is estimated that 137,000 km^2 of agricultural land (6.2%) needs local evaluation and remediation to ensure safe food production [14]. According to the USEPA (2019), there are currently 1344 sites in the USA that are designated on the Superfund National Priorities List [2], while there are 80,000 polluted sites in Australia.

Overall, soil pollution with toxic metals results in the reduced availability of cultivable land resources, decreased crop yield, contamination of agricultural products, and negative impacts on food safety and human health, which consequently impacts social and economic sustainability if not properly addressed [15]. In the last two decades, many studies have been conducted to investigate the pollution sources of toxic metals, identify indicators of soil pollution, and develop models to assess the impacts of soil pollution on ecosystem functions and human health. This paper was attempted to provide a brief review of recent progress in this field as shown in Figure 1 to shed light on the future management of soil pollution.
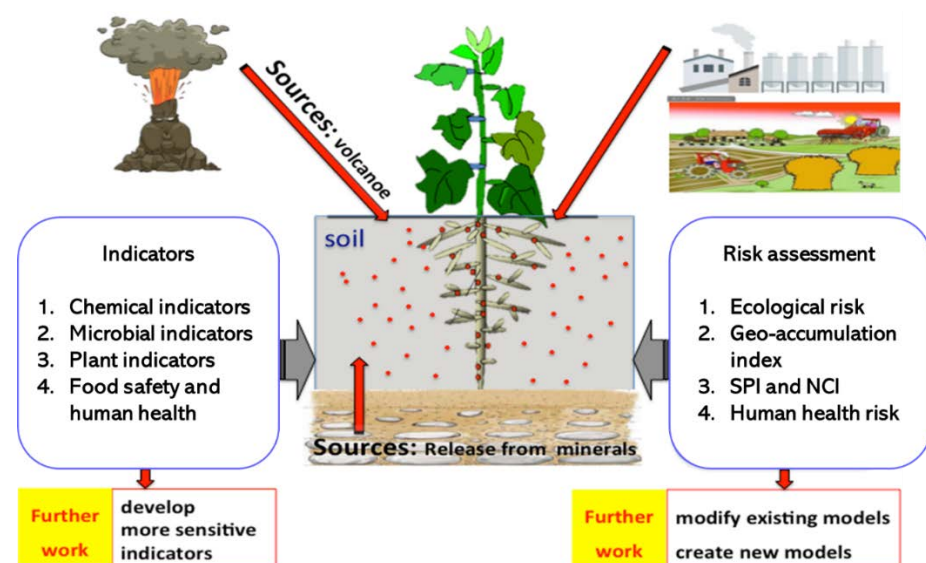

Figure 1. Map of framework on future management of soil pollution. SPI represents single-factor index and NCI represents Nemero comprehensive index.

2. Sources of Toxic Metal Pollution

The toxic metal pollution of soils can be induced from either geogenic processes and/or various anthropogenic activities. Geogenic processes include the erosion of parent rocks and volcanic eruption. Anthropogenic activities include industrial operations (dry and wet deposits, wastewater irrigation, mining, and smelting) and agricultural practices (fertilization, solid waste, and pesticides application). They could inevitably cause metal pollution to soil and the environment. There is no doubt that minimizing the sources of heavy metals is a successful method for enhancing the security and safety of soil and food.

2.1. Geogenic Processes

2.1.1. Parent Materials Weathering

Soils may inherit toxic metals from parent materials, such as metal-enriched rocks including black shale and serpentine [16,17]. It was reported the black shale in Ireland contained high quantities of Mo (200 mg kg^{-1}) and Se (220 mg kg^{-1}), respectively [18]. Earth crust includes igneous rocks (95%) and sedimentary rocks (5%); sedimentary rocks are constituted of 80% shales, 15% sandstones, and 5% limestone [19,20]. During soil development, Cu, Zn, and Cd are likely to concentrate in Mn oxides, whereas Pb tend to be enriched in Fe oxides and hydroxides. However, Cu, Zn, Cd, and Pb often coexist with sulfur, which could be quickly oxidized and released under superficial environmental conditions during mineral weathering. The iron and Mn oxides are slowly dissolved under reducing conditions and the sulfites of the elements are formed when sufficient sulfur is available. The European Union's Joint Research Centre (JRC) reported that toxic metal concentrations in soils varied according to parent materials [21]. For example, Cd is estimated 0.26–1.23 mg kg^{-1} in calcareous rocks, 0.11–0.94 mg kg^{-1} in crystalline rocks, but only 0.09–0.30 mg kg^{-1} in sandy deposits. Understanding the background level of toxic metals in soils is essential for the assessment of soil contamination and development.

2.1.2. Volcanic Eruption

Volcanic eruption is another geological process that releases toxic metals into soil. Gases from the eruption deposit toxic metals such as Cd, Hg, Cr, Cu, Zn, Mn, and Ni on soils. Deposits of metals and metalloids characterize the discharge regimes of active volcanoes [22]. On the sites of active volcanoes, the vents of fumaroles commonly contain metalloids (bismuth-Bi, As, antimony-Sb, tellurium-Te, and Se) together with a range of metals including Pb, Zn, thallium (Tl), and Hg [23]. Arsenic is deposited as As_2O_5 in fumarole sublimates because of high temperatures [24]. On the Tolbachik Volcano, Cu mostly occurs in the form of pseudolysonite ($Cu_3(VO_4)_2$) together with wolframite ($MnWO_4$) and elsewhere as rare Cu oxidized minerals [25]. Besides, metal-enriched sublimates are usually accompanied by a variety of hydrous aluminosilicates [26].

2.2. Anthropogenic Activities

2.2.1. Industrial Operations

- Dry and wet deposits

Toxic metal concentrations from dry and wet deposits varied with toxic metal nature and distance from point sources. For example, an increase in the Pb concentration in soil along highways has been attributed to emission from automobiles that use Pb-enriched gasoline in the past [16]. To understand the impact of traffic on soils, metals (Pb, Cu, and Zn) were determined in 225 samples in a grid system from an urban park [27]. High concentrations of Pb, Cu, and Zn were found in soils along the roadside and the accumulation in soils with distance from the road fitted an exponential model, indicating the strong influence of traffic pollution. Since the use of leaded gasoline in personal vehicles was banned in the developed and some developing countries, Pb pollution in roadside soil should be gradually controlled [28]. In some regions, manganese (Mn)-based anti-knock agents, methylcyclopentadienyl Mn tricarbonyl, are being used in gasoline [29]. However, the

background value of Mn in soil was higher as compared to Pb and, therefore, the influence of manganese-based anti-knock agents on roadside soil Mn accumulation is minimal [30].

- Wastewater irrigation

The chemical composition of a waste stream is dependent on its origin and the degree of treatment it has received. The heterogeneity of effluent waste streams is related to domestic, industrial activities (paper and printing manufacturing, timber processing plants, leather, and textile industries) and agricultural practices (dairy, poultry, meat, and vegetable processing). For example, Cu was reported at 0.002 mg L^{-1} in treated sewage [31], while 0.02–7.03, 0.26, 0.5–10.5 mg L^{-1} occurred in storm water, piggery effluent, and dairy effluent, respectively [32,33]. Arsenic was commonly presented in waste sludge and reported at 2.6, 43, 34.6, and 1.68 mg kg^{-1} in dairy cow slurry, beef cattle slurry, poultry litter, and swine slurry, respectively [34–36].

The input of metals through irrigation varies with locations and water sources. Natural water contains minimal toxic metals, usually at or below the critical values. However, industrial wastewaters usually contain significantly high concentration of toxic metals such as Cd, Ni, Cr, Pb, Zn, Co, Mn, and Cu, which may be added to soil via wastewater irrigation [37]. The repeated use of untreated wastewater may contribute to the accumulation of toxic metals in the soil and lead to a substantial build-up of toxic metals in the edible plant parts, eventually affecting plant growth, environmental quality, and human health. Meng et al. (2016) compared the toxic metals in surface soil irrigated with wastewater and clean water [38]. The averaged concentrations of Cd, Cu, Pb, Zn, Ni, Cr, As, and Hg in the soil irrigated with wastewater were 0.85, 41.2, 41.6, 276, 64.2, 91.2, 17.7, and 1.72 mg kg^{-1}, respectively, while those irrigated with clean water were 0.16, 26.9, 16.0, 70.5, 9.04, 8.62, 7.95, and 0.42 mg kg^{-1}, respectively.

- Mining and smelting activity

Mining and smelting are important economic activities, but also the largest sources of environmental pollution. They account for 48% of all pollutants released by the European industrial sector [39]. Large amounts of Pb, Zn, Hg, and Cd have been released into the environment in mineral processing activities, which have adversely affected the water and soil quality, plant growth, and food safety [40]. Lead, Cd, Cu, and Zn were the major pollutants due to Pb–Zn mining and smelting activities in China during the 2000–2009 period. According to reports, Yunnan, China's mining region had Pb and Zn concentrations that were 56 and 47 times, respectively, greater than the global average level [41,42].

The anthropogenic inputs of Hg into the environment through industrial emission is estimated at 3×10^6 kg $year^{-1}$ [43]. Mining–refining accounts for 12% of the global emission of Hg into air and is one of the largest sources of Hg in the environment [44]. The concentration of Hg in soil near Almade's Hg mining site was in a range of 0.13–2.695 mg kg^{-1} [45], which is much higher than that reported for unpolluted soils (0.01–0.50 mg kg^{-1}) [46]. In North America, sediments that have been deposited since industrialization were reported to have Hg concentrations 3–5 times higher than the background level [47].

2.2.2. Agricultural Practices

- Fertilizer application

The application of chemical fertilizers is a major contribution of toxic metals to soil. According to the report from the Ministry of Agriculture of China, 58.594 million tons of chemical fertilizer were used in 2017 [48]. The application of P fertilizers was reported to have resulted in soil contamination with toxic metals, particularly Zn, Cu, and Cd in the UK [49]. For example, P fertilizers contain varying concentrations of Cd, depending on the sources of phosphate rock [50]. In Western countries, 54–58% of soil Cd contamination is associated with phosphate fertilizer use [51]. For example, in Australia, P fertilizers manufactured from guano-derived phosphorites have had Cd contents of 300 mg Cd kg^{-1} and contributed 30–60 g Cd ha^{-1} to soils [52]. In China, the mean content of Cd was 0.75 mg kg^{-1} based on 1222 phosphate fertilizer samples during the 2006–2016 [53]. It is

reported that the concentrations of Cd in phosphorites (rock phosphates) can be as high as 500 mg kg^{-1} [54] and the concentration of As, Pb, and Hg in rock phosphate could be as high as 110, 17.2, and 0.42 mg kg^{-1}, respectively [55,56]. The excessive application of micronutrient fertilizers has resulted in considerable inputs of Cu or Zn and unacceptably high concentrations of Pb and Cd. A total of 28 tons of Cu are added to the soils in England and Wales each year through the addition of Cu fertilizer compounds to around 5% of cereal growing sites [57]. Additionally, certain customized micronutrient mixtures may contain large contaminants such as As (83 mg kg^{-1}), Pb (0.36%), and Cd (55 mg kg^{-1}) [58].

- Solid wastes application

The application of solid wastes in agriculture such as biosolids and farm manures has enhanced the toxic metal accumulation in soils, although its availability in soils may not change significantly within a short term [59,60]. Toxic metals in biosolids/farm manures in the USA, China, and some European countries were investigated [61–63] and the US–EPA and European countries also established a critical value of toxic metal for biosolids used in agriculture, although the standards vary between countries [64]. The median values of Zn, Cu, Pb, Cr, Ni, and Cd in some biosolids could reach 725, 463, 106, 40, 29, and 7 mg kg^{-1}, respectively, in the USA [61]. The repeated applications of biosolids/farm manures have been reported to increase the content of Cu, Zn, Ni, Pb, Cd, and Cr in soils [64]. Farm manures usually contained higher contents of As excreted from animals due to use of feed additives such as arsanilic acid, carbarsone, nitarsone, and roxarsone [63,65].

- Pesticides application

Metal-containing chemicals such as fungicides have been used in agricultural practice to prevent crop and fruit diseases for a long time. It was estimated that 1–2 kg ha^{-1} year^{-1} of Cu and As and 5–9 kg ha^{-1} year^{-1} of Zn and Pb entered the soils under fruit production due to the repeated spraying of chemicals [66–68]. Fungicides with high Cu contents are currently used for citrus disease prevention in the United State [69]. Thirty years old citrus grove soil was reported to contain 200–300 mg kg^{-1} extractable Cu, which is 10–15 times higher than that in non-citrus soils [70]. The use of Cu-based fungicides has accelerated the accumulation of Cu in vineyards, citrus groves, and other perennial crops. Soil contamination with Cu not only decreases crop production potentials due to soil quality degradation and phytotoxicity [71], but also leads to water pollution as increased amounts of Cu are transported to receiving water bodies through surface runoff or storm water [72,73].

3. Indicators for Toxic Metal Contamination of Soils

3.1. Chemical Indicators

The total concentration of metals and metalloids is the most commonly used chemical indicator of soil pollution. Most national and international guidelines or standards for toxic metals in soil are based on the total concentration and the regulatory standards of toxic metals in agricultural soils differ among the countries/regions [74–78]. The total concentration reflects both geological origins and anthropogenic inputs of toxic metals in the soil. However, the mobile or bioavailable content is less than 5% of the total content and, therefore, the total concentration may not indicate the actual bioavailability or mobility of the metals in soils [16]. Considering the effect of soil pH and redox on the solubility of toxic metals in soil, some countries such as China have modified the total concentration standards of toxic metals by accounting for soil pH and land use. For example, the Cr standard in upland was 200, 250, and 300 mg kg^{-1}, respectively, when the soil pH was <6.5, 6.6–7.5, and >7.5 and was 250 and 200 mg kg^{-1}, respectively, in paddy and upland (pH 6.6–7.5) soils in China.

Recently, studies have been conducted to identify labile or bioavailable pools of trace metals in soils as indicators of soil contamination. For toxic metals, selective extraction methods are applied for assessing their environmental impact. One of the most widely used approaches is the single extraction procedure [79] and extractable metals could represent

their bioavailability or toxicity. Several extraction procedures were proposed to estimate the labile toxic metals in soil based on their water solubility or chemical association with soil constituents [79]. Based on the reaction mode, the extractants include (1) acids (e.g., HCl, HNO$_3$); (2) chelating agents (e.g., EDTA and DTPA); (3) buffered salt solutions (e.g., NH$_4$OAc); and (4) unbuffered salt solutions (e.g., CaCl$_2$ and NH$_4$NO$_3$) [80]. Single-step chemical extraction is the most useful tool for estimating the number of metals in soil that are readily available, including exchangeable pools and water soluble. As the extractable metals in soil are closely correlated with the plant uptake [81,82] or loads in runoff water [72,83], it is often referred to as the available number of metals or indicators of metal availability in soil. In a soil-crop rotation trial, Jing et al. (2008) reported that among the four extraction procedures (HCl, NH$_4$OAc, DTPA, and CaCl$_2$), 0.1 mol L^{-1} HCl extractable Hg provided the optimum indication of plant Hg uptake [81].

Metal fractionation in soil can improve the understanding of their association with soil constituents and release characteristics when soil and environmental conditions change. Generally, soil metal is fractionated into water soluble, exchangeable, organically bound, carbonate bound, oxides bound, and residual pools using consecutive extractions with selective chemical reagents [67,82,84]. The advantage of sequential extraction is the improved phase specificity and providing information on the potential mobility or bioavailability of toxic metals in soil [85]. Li et al. (2009) determined the fractions of Hg in soil from a mining deposit following the European Community Bureau of Reference (CBR) protocol and reported that a large proportion of Hg remained in the residual fraction, which has less effects on soil biota and less potential to contaminate food chains through plant uptake [86]. Both single extraction procedure and CBR protocol are useful for assessing the bioavailability of toxic metals in soil. In order to assess the risk of human health from exposure through the ingestion pathway, it is necessary to determine bio-accessible fractions using simulation human gastrointestinal systems [87].

3.2. Microbial Indicators

3.2.1. Microbial Biomass and Microbial Quotient

Microbial biomass (C$_{mic}$) is an early indicator of toxic metal contamination, which represents a part of the living biota in soil [88,89]. Once excessive amounts of toxic metals enter soil, microorganisms are the first biota killed or biochemically disabled [90,91]. The microbial biomass in agricultural soils applied with biosolids was reported to be smaller than that in the soils receiving farmyard manure and decreased with the increase in EDTA-extractable Ni and Cu over 20 years [61]. An additive adverse impact on the C$_{mic}$ was reported when a high concentration of Zn and Cu coexisted and Cu decreased C$_{mic}$ more than Zn at a similar concentration [92]. The toxic effect of metals on soil C$_{mic}$ was also affected by the soil texture, probably attributed to the differences in toxic metal adsorption and bioavailability among different soils. It is reported that the soil texture was positively linked with Cd toxicity. For example, clay loam and loam soils had higher levels of soil microbial biomass and enzyme activities than sandy loam soil [93].

The microbial quotient was defined as the ratios of microbial biomass C/soil organic C. It was shown to be negatively influenced by increasing concentrations of toxic metals, depending on the variation in the chemical composition of the source, amount, and types of toxic metals and the duration of exposure [94,95]. For example, the negative effects on the microbial quotient were enhanced with increasing Zn solubility, but the effect on the ratio of microbial biomass N/total N was smaller [96]. However, Dai et al. (2004) found that the microbial quotient did not exhibit significant changes under the stress of heavy metal (Zn, Cd, Pb, and Cu) [97]. In brief, there is no clear and consistent change of microbial biomass or related ration in response to heavy metal and either of them can be used as a separate microbiological indicator to toxic metal contamination.

3.2.2. Respiration Rate and Metabolic Microbial Quotient

The basal respiration rate (qCO_2, mg CO_2-C kg^{-1} per day) is a bioindicator to reflect microbial activity. The metabolic microbial quotient (MMQ) is defined as the ratios of qCO_2/C_{mic}. Both were reported to significantly increase with the increasing concentration of toxic metals in soil. With the increase in the heavy metal contamination in the sampling area, the six enzyme activities and C_{mic} decreased, but the qCO_2 increased according to the investigation of heavy metal pollution on five different land use types [98]. This indicates that the energy utilization of the microbial metabolic process is stressed by toxic metals, thus transferring more of a quantity of C incorporated into the metabolic maintenance [99]. Whereas the ratio qCO_2/C_{org} slightly decreased when contaminated with toxic metals, indicating microbial toxic stress due to toxic metals [89]. Romero-Freire (2016) studied seven different soils with different pollution levels of As, Pb, Zn, and Cu and the results showed that SBR is not a reliable indicator of Pb, Zn, or Cu pollution in soils with a lot of organic carbon, but presented good sensitivity in low organic-matter content and acidic pH soils [100].

3.2.3. Microbial Community Structure

The microbial community structure varied with nutritional or environmental changes and more sensitive microbial populations disappeared under changed conditions [16,101]. The changes in the microbial community structure were regarded as a biological indicator of heavy metal contamination in soils, which could be determined by physiological, biochemical, or molecular techniques [102]. An increase in toxic metal concentrations in soil decreased biomarkers of actinomycetes and fungi but increased the relative proportion of bacteria [103], suggesting that bacterium is more resistant to toxic metals than other microbial populations. However, Zheng (2019) obtained a contrasting result, which indicated the number of bacteria and actinomycetes was significantly decreased in toxic metal contaminated soils, while the fungal counts were not significantly changed [104].

3.2.4. Soil Enzyme Activity

Soil enzymes are mostly excreted from soil microbes and participate in many biogeochemical processes, such as nutrient cycling, soil structure maintenance, and pollutant detoxification. The soil enzymes are sensitive to disturbance in the soil ecosystem and have been widely used as bioindicators for the toxicological influences of pollutants. The most commonly determined enzyme indicators include urease, dehydrogenase, phosphatase, sulfatase, glucosidase, and protease activities, average microbial endpoint (AME), and fluorescein diacetate (FDA) hydrolysis [94,105]. It is reported that Cd decreased 25.52–34.89% of the soil catalase activity, while Hg (30 mg kg^{-1}) decreased 76.50–89.88% of the soil urease activity and 85.60–92.92% of the soil dehydrogenase activity, respectively [104]. Khan et al. (2010) evaluated changes in the activities of phosphatase and urease in the Cd- and Pb-contaminated soil [95]. The enzyme activity was reduced to 36% in the soil received 5 mg kg^{-1} Cd or 500 mg kg^{-1} Pb than the control and the highest inhibition occurred after 2 weeks of incubation. Fluorescein diacetate (FDA) hydrolysis by proteases, lipases, and esterase is used to determine the quantity of active fungi and bacteria. The hydrolysis of FDA was reported to decrease with increasing loading of Pb in an acidic sandy soil. However, the sensitivity of FDA hydrolysis to toxic metal pollution varied with the soil type [105].

3.2.5. Average Microbial Endpoint

A lack of correlation may be expected more frequently in the field than in laboratory studies, particularly at low levels of pollution, due to the high soil heterogeneity and the complex relationships that link soil chemical, physical, and biological parameters.

The comprehensive variables (such as the average microbial endpoint, AME) consider the response of many microbial functions or characteristics, thus decreasing the chance of

site-specific effects that may induce anomalous responses on a single parameter used as a descriptor.

The AME index is calculated for each site as follows:

$$\text{AME} = \sum_i \frac{N_{ij}}{n_p} \text{ with } i = 1, \ldots, n_p \text{ and } j = 1, \ldots, n_s \qquad (1)$$

with

$$N_{ij} = \frac{P_{ij}}{P_{imax}} \qquad (2)$$

$$P_{imax} = \text{MAX} \left(Pi1, Pi2, \ldots, Pin_s \right) \qquad (3)$$

where N_{ij} is equal to the normalized value of ith parameter P (microbial parameter or endpoint) measured in the jth site; n_s = number of compared sites and n_p = number of microbial parameters or endpoints (P) measured.

Expressing the microbial response as a comprehensive parameter or endpoint provides an expression or a snapshot of the overall microbial functionality in comparative studies, which may not have an obvious single endpoint. The AME index represents the mean response of the microbial parameters under consideration. Therefore, as an "average", it can improve the representation of the response of the whole microbial community. The more parameters that are evaluated, the wider the possible range of microbial functions could be. The AME index is useful in the field as a general biomarker of microbial functionality in comparative studies assessing the impact of different types of pollution or the effects of different levels of the same pollutant on soil quality or to follow the soil response to remediation programs [94].

3.3. Plant Indicators

Excessive toxic metals in soil could negatively affect plant growth and crop production [106–108]. For example, heavy metals can inhibit plant growth and decrease chlorophyll content and biomass productivity [109,110]. Besides, these heavy metals can be easily transferred from soil to plants and accumulate in edible parts, consequently increasing dietary exposure to consumers even at sub-phytotoxic levels [111]. Plants concentrate metal elements in their above ground parts, which is a sign that soil heavy metal concentrations are high. For example, Cd often limit plant growth by altering leaf internal structures and reducing cell wall extensibility and relative water content [112]. Pb can decrease the efficiency of PSll electron transport, the total chlorophyll concentration, and the leaf expansion [113]. The accumulation characteristics of Cd are associated with both soil properties and plant species. It was reported that Cd in metalliferous mining and smelting soil was more likely accumulated in vegetables, as compared to soils treated with biosolids [54]. Studies indicated that the Cd concentration in plants varied widely among the crops [111,114]. Among soil properties, soil pH is one of the major factors affecting Cd availability in soil [115]. Emulative toxic metals, such as Cu, Ni, Se, and Mn, can reduce Cd uptake by plants [116]. Other soil properties, such as soil adsorptive capacity and the redox conditions, also affect toxic metal transferring from soil to plant [117,118]. Overall, heavy metal toxicity has numerous direct and indirect effects on a variety of physiological functions and the morphology of plants, which are reflected in the changes of leaf functional traits. Plant indicators bring new opportunities for characterizing heavy metal contamination, without being limited by time-consuming soil sampling and processing [119].

3.4. Food Safety and Human Health

Food is the major cause of Cd exposure to humans (up to several hundred $\mu g \text{ day}^{-1}$) for the general population except for smokers [11]. Toxic metal speciation in plant tissues is an important factor affecting its accumulation in the human body. Aziz et al. (2015) studied the bio-accessibility, bioavailability, and toxicity of toxic metal in Chinese cabbage

(*Brassica rapa*) for humans using in vitro tests [120]. Human intestinal epithelial cell line (*Caco-2*) was used to mimic the process of intestinal cell retention and transport. The results showed that Cd in Chinese cabbage contributed to total the daily intake of Cd by humans. Besides, potential links have been reported between Cd levels in topsoil and cancer incidence in Europe and cancer incidence increased with the increase in Cd concentrations in topsoil [11]. Once the grazing land is contaminated by toxic metals, the consumption of cattle offal could result in a significant health risk to humans. It is reported that meat, offal, fish, eggs, and dairy products contain Cd up to 40, 1000, 20, 30, and 30 $\mu g\ kg^{-1}$, respectively [11]. The cadmium concentration in milk was as high as 30 $\mu g\ L^{-1}$ after an intravenous injection of a tracer dose of $CdCl_2$, which is approximately 15 times higher than the guideline values of drinking water [121].

4. Risk Assessment

4.1. Standards

There are two management strategies on soil pollution: one is based on critical levels and the other according to risk assessment. An international trend is to protect the soil quality based on ecology and human health. The evaluation method is different between the ecological and human health risk assessment. The Department of Environment and Conservation in Australia provided ecological investigation levels (EILs) and health investigation levels (HILs) and the risk assessment should be applied when toxic metal concentration in the soil is above investigation levels.

4.2. Methodology

4.2.1. Ecological Risk

Ecological Investigation Levels are based on the toxicity to plants, animals, and microorganisms, as well as background soil survey data. The Health Investigation Levels are based on "phytotoxicity and threshold levels for uptake of contaminants, which may result in impairment of plant growth or reproduction or unacceptable residue levels". The US EPA developed the Ecological Soil Screening Levels (Eco-SSLs) for superfund sites management (https://www.epa.gov/ecotox, accessed on 15 August 2022). They are used to protect ecological receptors such as animals, plants, and microbes. If concentrations of toxic metals are higher than the Eco-SSLs, the ecological risk assessment should be conducted [122].

- Geo-accumulation index

Geo-accumulation (I_{geo}) was initially proposed to assess the sediment pollution levels [123] but is also applied to assess toxic metal pollution levels in soil. I_{geo} is computed by the following equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right) \tag{4}$$

where C_n represents the toxic metal concentration in soil, B_n is background concentration of toxic metal in shale, and the factor 1.5 is used for compensating B_n due to lithogenic effects. The geo-accumulation index is classified into seven or five grades. According to the procedure of I_{geo} determination, the concentration of toxic metals in soil of highest grade is more than 150 folds of the background value. For avoiding the lower differentiation in assessment, the seven-grade classification is usually selected for assessing the toxic metal contamination in soils. "$I_{geo} \leq 0$" represents practically uncontaminated, "$0 < I_{geo} < 1$" represents from uncontaminated to moderately contaminated, "$1 < I_{geo} < 2$" represents moderately contaminated, "$2 < I_{geo} < 3$" represents from moderately to heavily contaminated, "$3 < I_{geo} < 4$" represents heavily contaminated, "$4 < I_{geo} < 5$" represents from heavily to extremely contaminated, and "$I_{geo} > 5$" represents extremely contaminated.

- Single-factor index (SFI) and Nemero Comprehensive Index (NCI)

The single-factor index is calculated as: $P_i = C_i/S_i$, and Nemero comprehensive index is calculated as:

$$P = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n} P_i\right)^2 + [\max(P_i)]^2}{2}} \tag{5}$$

where C_i (mg kg^{-1}) is concentration of toxic metal i; Si (mg kg^{-1}) is background concentration of toxic metal i [124]. The NCI is classified into five levels: excellent ($P \leq 0.7$), clean ($0.7 < P \leq 1.0$), slightly polluted ($1 < P \leq 2.0$), moderately polluted ($2.0 < P \leq 3.0$), and heavily polluted ($P > 3.0$).

4.2.2. Human Health Risk

The toxic metals in soil can pose a threat to human health via direct exposure (ingestion, dermal contact, and inhalation of soil particles) or indirect exposure (groundwater contaminated by toxic metals leaching from the soil profile, surface water contaminated by dusts or run-off). Exposure also occurs due to hazardous dusts from the reworking of soils, as in contaminated site remediation [125]. They can accumulate in the human body via direct ingestion, dermal contact absorption, and inhalation [126,127]. The drinking of water and inhalation of soil particles are the major pathways for human exposure to toxic metals [128]. Besides, toxic metals can build up in the food chain then enter the human body through food consumption [128,129]. It has been reported that As > Pb > Cu in the exposed soil are the major health risks and account for 81%, 12%, and 5% and 77%, 12%, and 8% of hazard quotients for children and adults, respectively [130].

- Ingestion

$$CDI_{ingest-soil} = \frac{CS \times IRS \times EF \times ED}{BW \times AT} \times CF \tag{6}$$

- Dermal contact

$$CDI_{dermal-soil} = \frac{CS \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \tag{7}$$

- Diet

$$CDI_{vergetable} = \frac{C_{vegetable} \times IR_{vegetable} \times EF \times ED}{BW \times AT} \tag{8}$$

where *CDI* is chronic daily intake; *CS* is exposure-point concentration: mg kg^{-1}; *IRS* is ingestion rate: 100 mg d^{-1}; *EF* is exposure frequency: 350 d/a; *ED* is exposure duration: 30 a; *CF* is unit conversion factor: 10^{-6} kg mg^{-1}; *BW* is body weight; *AT* is averaging time for non-carcinogens: $365 \times ED$ d; *AT* is averaging time for carcinogens: 365×70 d; *SA* is exposed skin area: 5700 cm^2 [131]; *AF* is adherence factor: 0.07 mg cm^{-2}; *ABS* is dermal absorption fraction: 0.03 (As) or 0.001 (other metals); and $IR_{vegetable}$ is ingestion rate: 0.345 kg d^{-1} [132].

If toxic metals in soil exceed screening assessment levels, a complete investigation and human risk assessment should be conducted to determine whether the levels present are safe or likely to pose an actual risk. The US EPA's methodologies are for assessing the potential risks to human health, including carcinogens and non-carcinogens, and they have been widely accepted worldwide [133]. However, screening assessment levels were different between countries and the risk may vary with specific sites because of different site conditions, exposure ways, susceptible people, etc. For example, according to the assessment results from 402 industrial and 1041 agricultural sites in China, pollution and risks in industrial regions were severer than agricultural regions and children were more likely to be affected by toxic metal pollution than adults [134]. Further investigation should take consideration of comparative and comprehensive assessments including background concentrations and site-specific factors that may influence contaminant availability.

5. Prospects and Future Research

Soil pollution by potentially toxic metals has become a worldwide environmental issue. Being persistent, mobile, and bioaccumulation, toxic metal contamination negatively affects soil and environmental quality, impacts food quality and security, and poses a threat to human health. Both geogenic processes and anthropogenic activities contribute to increased concentrations of toxic metals in soil. It is critical to control the inputs of toxic metals from industrial sources and agricultural practices. Many indicators are available for identifying polluted sites and monitoring remediation efficiency. So far, the total and/or total recoverable concentration is still most widely used for the assessment of toxic metal contamination and subsequent management of contaminated soil.

Further work is needed to improve soil contamination diagnosis, modeling, and regulatory standards, as well as remediation strategies. Firstly, it is necessary to develop more sensitive indicators such as bio-indicators and the available concentration of toxic metals in soil. A cost–benefit diagnosis sets the foundation for soil contamination management. Secondly, although several models have been developed for assessing soil pollution by toxic metals, each has its own strength and weakness. More efforts are needed to modify existing models and create new ones applicable to eco-system services. Thirdly, the guidelines established by individual countries worldwide to control the heavy metal pollution are not consistent or standardized, therefore efforts need to be performed to develop international standards for soil pollution with potentially toxic metals. In this case, various environmental systems, climatic, geological, and hydrological conditions, and even the political factors, should be considered in the establishment of regulations. Furthermore, comparative evaluations are required to select cost-effective remediation strategies. Although a variety of strategies, including physical and thermal desorption and chemical and biological remediation, have been used in soil remediation, they are limited in terms of cost and efficacy. It is worth pointing out that phytoremediation is gaining interest from numerous researchers due to its advantages of cost-effective and eco-friendly remediation methods. Moreover, cutting-edge technologies may be incorporated into existing technologies to improve remediation efficiency and guarantee food security.

6. Concluding Remarks

With rapid industrialization, soil contamination by toxic metals has been accelerated worldwide. The present review discussed the fundamentals of sources, indicators, and the assessment of soil contamination by potentially toxic metals. Geogenic processes and anthropogenic activities are two important sources of soil pollution. Soils may inherit toxic metals from parent materials; however, most soil pollutions result from industrial and agricultural activities. Contamination by metals can be indicated by the changes in chemical, biochemical, and microbial properties of soils and plant responses. The total concentration of toxic metals in soil is still the most widely used indicator for risk assessment although extractable amounts have been reported to be more closely related to plant uptake. Several models have been proposed for assessing soil contamination by toxic metals, but none of them are commonly accepted for application to a wide range of soils. The review highlights the need for systematic studies to improve soil contamination diagnosis, modeling, regulatory standards, and remediation efficiency.

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